

Vincent Salters Research Projects

Speciation of Metals and Nutrients in Natural Waters

This project is done in collaboration with Dr. Landing (Oceanography), Dr. Cooper (Chemistry) and Dr. Marshall (NHMFL and Chemistry). There is mounting evidence that an ecosystem's response to chemical stresses such as excess nutrients or heavy metals is first manifested at the lowest levels in the food web, i.e. in the bacteria, phytoplankton, and other micro-organisms. The response of these primary consumers is related to the chemical form, or speciation, of pollutants, and their stress is ultimately reflected farther up the food web in the macro-organisms. By knowing the chemical speciation of environmental stressors at the molecular level, we will be able to understand their bioavailability and ultimate effect on overall ecosystem health before dramatic changes occur. In addition, treatment ponds and wetlands can be engineered more efficiently if the biochemical processing of discrete pollutant species is known at the molecular level. Here we propose to perform speciation studies. Subsequently, the result of these studies can be combined with incubation experiments to determine bioavailability.

In natural waters complexation with Dissolved Organic Matter (DOM) is an important factor in determining bioavailability. Despite its recognized importance in determining the bioavailability and geochemical fate of chemical contaminants, little is known about the relationship between structure and composition of aquatic DOM and its biogeochemical reactivity. This lack of knowledge is mostly due to a lack of suitable analytical techniques to attack the problem. We propose the application of high resolution mass spectrometric techniques for characterizing the composition and structure of the principal nutrients within DOM (dissolved organic nitrogen; DON, and dissolved organic phosphorus, DOP) using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS). We also propose to quantify the amount of radionuclides and metal ions associated with the individual groups of DOM by high resolution Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. And thirdly, we will determine the functional groups responsible for metal binding using Electron Paramagnetic Resonance (EPR) techniques. These three techniques will provide a unique perspective on DOM and its behavior in waters. We propose to perform demonstration studies in areas where potential for funding is greatest: characterization of Dissolved Organic Nitrogen (DON) and Dissolved Organic Phosphorus (DOP); and speciation of radionuclides and Cu and Fe with DOM.

Hf-isotopes in Mantle Materials

Hf-isotope studies of mantle materials with the goal to identify and characterize recycled material in the mantle. The terrestrial array indicates that the Lu-Hf and Sm-Nd system are well correlated and regression of the array leads to $\varepsilon_{\text{Hf}} = 1.35 \varepsilon_{\text{Nd}} + 3\varepsilon_{\text{Hf}}$ (Vervoort et al., 2000; Vervoort et al., 1999). We will test this excellent correlation between Nd and Hf isotopic compositions by analyzing materials from "extreme" isotopic or trace element environments. The Hf and Nd isotope systematics will provide

interesting and powerful information in places where the Nd and Hf systems are differently correlated. Lu-Hf-Sm-Nd characteristics of pelagic sediments, oceanic crust, depleted oceanic lithosphere as well as carbonatites imply evolution lines that have a different slope than the terrestrial or ocean basalt array. These distinctive trace element and Hf-Nd isotopic characteristics allows for relatively easy recognition of these components in oceanic basalts as well as good estimates on the duration of isolation of these components (mantle heterogeneity). The fact that the oceanic basalt array is so well defined indicates that processes or components that would move mantle compositions off the array are either insignificant in volume or are mixed back in on relatively short timescales. We will test sediment involvement by major and trace element as well as isotope characterization of basalts from Walvis Ridge and from the Samoan Island chain which exhibit some of the most enriched trace element and isotopic characteristics of the oceanic mantle. The results will provide strong constraints on the source of the enrichment (i.e. sediment, carbonatite etc).

Pyroxenites and eclogites have been proposed by many as the source for the enriched trace element and isotope signatures in the basalts. Pyroxenites are thought to represent either trapped melts or recycled crustal material. The existence of pyroxenite in the melting region has important consequences for our estimates of degree and depth of melting as well as melt transport times. It is therefore extremely important that we are able to recognize melts derived from pyroxenites. However, very few pyroxenites have been characterized for isotopes and trace elements. I propose to analyze pyroxenite and eclogites from a variety of settings to determine the systematic chemical variations in pyroxenites in both trace elements and isotopes. Determining the systematic variation in pyroxenites and the differences with lherzolites will allow us to determine the composition of pyroxenite derived melts. Furthermore, identification of recycled oceanic crust in pyroxenite and determination of the age of this material are important for our understanding of the time scale of mixing. Hf-isotopic compositions are crucial indicator of the recycled component as well as determining its age and thus the determination of the “survival chances” of recycled material. Furthermore, analyses of mantle peridotites are needed to test whether the Hf-Nd isotope correlation observed in basalts can be extended to their source materials and to determine to what extend there is a need to call upon pyroxenite components to explain some of the heterogeneity.

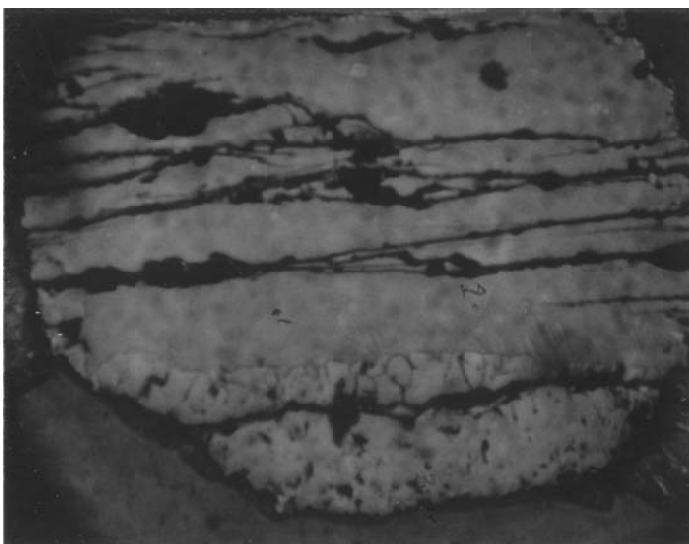
Near Mantle Solidus Trace Element Partitioning at Pressures up to 3.4 GPa

This is a collaborative project with Dr. Longhi at [Lamont Doherty Earth Observatory](#) at Columbia University. We present new experimental partitioning data for a range of petrogenetically important elements up to pressures of 3.4 GPa which is an extension of our previous study (Salters and Longhi, 1999). The experiments are designed to mimic melting beneath mid-ocean ridges. The available data indicates that the partition coefficients are pressure, temperature and composition dependent. Therefore, if melt is extracted continuously during the adiabatic rise of mantle material, knowledge of partition behavior over the appropriate range of pressure, temperature and composition is required. For this purpose, we have parameterized the partitioning behavior of the REE, Hf, Zr, U and Th based on a simple thermodynamic model. This parameterization

shows that although it cannot be used for retrieving thermodynamic constants yet, the parameterization does yield a description of the partitioning behavior, which is useful for modeling decompression melting.

Our parameterization shows that on the peridotite solidus the partitioning of trace elements is strongly dependent on the Ca and Al-content of the clinopyroxene. However, REE are always incompatible in cpx on the peridotite solidus at pressures up to 3.4 GPa. For garnet the data indicates that the heavy REE partition coefficients decrease with increasing pressure. Our data indicates that Pb is more incompatible than Ce and in garnet Ce and Pb have similar partition coefficients. Therefore, in order to explain the near-constant Ce/Pb ratios in MORB and OIB a residual phase with high Pb partition coefficients is required. It is suggested that sulfides are the most likely phase that buffer the Pb content in the melt.

Clinopyroxene on the peridotite solidus is unable to fractionate U from Th significantly, garnet can fractionate U from Th effectively. Therefore, if the ^{230}Th -excesses in basalts are a melting phenomenon than melting with garnet residual is required. Previous studies showed that the coupled Sm/Nd and Lu/Hf fractionation in MORB require residual garnet. The new partitioning parameterization of the REE and Hf is in agreement with these previous studies.



Photomicrograph of Experimental run product.

Run product of experiment TM295-5 which is typical for our run products. Crystals are concentrated at the bottom and comprise of less than 30% of run products. Light and dark gray areas in crystal pile are ol and opx, respectively. Light and dark areas above the crystal pile are diffuse quench crystals and glass, respectively. There is no difference in composition between quench areas and glass at the scale of a 15 micron rastered electron beam. Field of view approx. 2mm

Assessing the Presence of Garnet Pyroxenite in the Mantle Sources of Basalts: Hafnium-Neodymium-Thorium Isotope Evidence

The existence of an enriched component in the mantle with a pyroxenitic or eclogitic composition and its importance for basalt genesis has been discussed for over two decades. Inferences about the depth of melting as well as the dynamics of melting based on the presence of garnet and the location of the spinel-garnet transition are different if garnet-pyroxenite is present in the peridotitic mantle. Trace element partition coefficients are dependent on composition and the differences between garnet-pyroxenite and peridotite are large enough to produce significant differences in trace element fractionation between melts derived from these different lithologies. Melts derived from garnet-pyroxenite or eclogite-bearing sources will have small or no ^{230}Th -

excesses largely independent of melting and upwelling rate. Melts derived from garnet-peridotite will have significant ^{230}Th -excesses which are dependent on melting and upwelling rate. We show that the combined hafnium-neodymium-thorium (Hf-Nd-Th) isotope and trace element data can distinguish between melts derived from peridotitic



and pyroxenitic or eclogitic sources. We also present new Hf-isotope data for Hawaiian basalts, and use the combined Hf-Nd-Th isotope and trace element systematics to argue against the existence of garnet-pyroxenite or eclogite in the source of Hawaiian basalts. It is especially the large variation in degree of melting for relatively constant isotopic composition that allow us to rule out garnet-pyroxenite in the source of the Hawaiian basalts.

Temporal Chemical Variations within Lowermost Jurassic Tholeiitic Magmas of the Central Atlantic Magmatic Province

The [Central Atlantic Magmatic Province](#) (CAMP), which covers more land area than any other large igneous province (LIP), marked the beginning and early stages of the Pangaeian breakup. The CAMP surrounds the Central Atlantic in eastern North America, northeastern South America, western Africa, and southwestern Europe. It apparently covers over $7 \times 10^9 \text{ km}^2$ and was active for no more than 4 Ma. Virtually all CAMP rocks are mafic tholeiites, and include both intrusives and extrusives. The most extensive intrusives are diabase (dolerite) dikes, which occur in three main swarms on Pangaea: NW-, NE-, and NS trending. These mafic tholeiites, including all intrusives and extrusives, can be classified into three magma types based on their Ti contents: low-Ti (LTi), intermediate-Ti (ITi), and high-Ti (HTi). The NE swarm contains primarily the ITi magma type, whereas the NW swarm is relatively heterogeneous and contains all three types. The N-S swarm contains highly evolved (high-Fe) quartz tholeiites in North America and ITi rocks in South America. Based on both compositions and attitudes, these dike swarms can be correlated across the Atlantic. For example, the HTi type of the NW swarm is most common in Liberia, and across the Atlantic in adjacent (on Pangaea) Surinam and French Guyana.

The available chemical data do not indicate a simple petrogenetic history for CAMP, and arguments can be made for both “active” and “passive” models of magma evolution. These complications may in part be due to a lack of sufficiently high-quality geochemical and geochronological data in some critical areas, but they also may be due to a genuine greater degree of complexity for CAMP’s evolutionary history compared to other, smaller LIPs. For example, the relation between known ages and estimates of both depth and degree of melting is contradictory in comparison to other LIPs. Some patterns within the CAMP are apparent, however. The most interesting, and

potentially significant, pattern is a temporal symmetry of dike and magma characteristics; i.e., characteristics were apparently similar in the early and late stages of the evolution of the CAMP, but quite different in the middle stage. This symmetry almost certainly has a bearing on the tectonic history of the Pangaeian breakup, but at this time its significance is not clear. For example, the change of some characteristics with time support an active plume model; the change in others support a passive model.

The two principal magma types within the CAMP, LTi and ITi, were apparently derived from lherzolitic mantle sources that were compositionally similar that contained both continental lithospheric and asthenospheric components. Compared with other large igneous provinces the CAMP basalts show depleted geochemical characteristics. Compositional differences between them are primarily due to differences in depth and degree of melting; LTi represents the deepest and greatest degrees of melting. We will show that the estimates of degree and depth of melting based on major- and trace-element characteristics can provide important constraints on the mechanism for continental break-up associated with the CAMP. The temporal progression of the chemical characteristics indicate deeper melting with time, which is consistent with a shallow (such as crustal thinning) and passive origin for the break-up of the Pangaeian continent.

Determining the Mineralogy of the MORB Source through Nd-isotope Analyses on Abyssal Peridotites

Interpreting the chemical and isotopic systematics of MORBs in relation to details of the melting process and the physical conditions under which melting takes place hinges on the assumption of compositional similarity or regularity between all MORB sources (Langmuir et al., 1992; McKenzie and O'Nions, 1991; Salters and Hart, 1989; Spiegelman and Elliott, 1993). For example, the interpretations of regular variations in Na_8 and Fe_8 versus axial ridge depth, thought to reflect a deeper initiation of melting and higher extents of melting beneath shallow ridges (Klein and Langmuir, 1987), are only valid in the context of chemically and mineralogically homogeneous source mantle. Similarly, observed correlations between $^{230}\text{Th}/^{238}\text{U}$ or $\delta_{(\text{Lu}/\text{Hf})}$ and $\delta_{(\text{Sm}/\text{Nd})}$ and ridge depth only bear directly on the physics of the melting process if mantle composition does not vary systematically with ridge depth (Bourdon et al., 1996; Salters, 1996). In this context, chemical or mineralogical homogeneity of the source is not required in the strictest sense, due to the scatter in the correlations between chemical parameters and ridge depth. However, *systematic* mineralogical or compositional source variations with ridge depth, or with Na_8 , Fe_8 , $\delta_{(\text{Lu}/\text{Hf})}$, $\delta_{(\text{Sm}/\text{Nd})}$ or $(^{230}\text{Th}/^{238}\text{U})$ (as, for example, the ridge approaches a hot spot), would essentially undermine the basis for the accepted interpretations of the correlations (Zindler and Salters, 1995). Thus, those aspects of MORB chemistry that are related to mixing between hotspot and "normal" MORB sources may not be used in a straightforward manner to infer variation in the depth or extent of melting or the shape of the melting regime. This is especially true where the plume component comprises pyroxenitic instead of peridotitic lithologies. In this case it becomes difficult, if not impossible, to draw simple inferences concerning the depth or extent of melting.

To maximize the information obtained from chemical and isotopic parameters with regard to the depth and extent of melting in the MORB mantle, the issues of source

chemical variations and the possible presence of garnet-bearing mafic material in the MORB source must be resolved. We propose that these questions can be addressed by investigating the presence or absence of an enrichment signature in the Nd isotope ratios of clinopyroxene (cpx) from s (APs). The study we propose is a “pilot” study to show that (1) the analyses is technically feasible and (2) the information obtained can be used to unravel the history of the MORB source. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of associated ridge basalts will be used as a measure of the integrated melt signature at the ridge. If the isotopic and chemical enrichment observed in MORBs near hotspots derives from recycled pyroxenitic material that retains its lithologic character in MORB source mantle, then cpx from APs would not necessarily be expected to display the chemical and isotopic trends of associated basalts. However, if the enriched character of the mantle is indigenous to the peridotite, then the cpx should display basalt-like trends toward increasing enrichment near hotspots. In the first case, inferences of the physical conditions of melting based on $\delta_{(\text{Lu}/\text{Hf})}$, $\delta_{(\text{Sm}/\text{Nd})}$ or $(^{230}\text{Th}/^{238}\text{U})$ would have to be reevaluated.

This project focusses on Nd isotope ratios because of the relative ease with which they can be measured in peridotitic cpx (Richardson et al., 1985; Zindler and Jagoutz, 1988), and the fact that the information from the Nd should be sufficient to achieve our goals.

References

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Determining the $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of bulk Earth through studies of meteorites

This project is done collaboration with Janne Blichert-Toft (ENS-Lyon, France, Jon Patchett and Jeff Vervoort (U. Arizona).

Patchett and Tatsumoto (1980) made the first estimate of the bulk Earth Hf-isotopic composition on data on achondrites. This early state-of-the-art work was hindered by the low precision of the measured isotope ratios as the ionization efficiency of TIMS is poor. In addition, this early work was done on achondrites which are differentiated meteorites and not the pristine material of the solar system which is better represented by chondrites. Hf-isotopes analyses on chondrites (Patchett and Tatsumoto, 1981) had rather large errors and required large corrections because the low concentrations of the chondrites required ion counting. However, the chondrite bulk Earth value was within error of the value derived from achondrites. Despite the obvious limitations of this early work it took more than 15 years before we could even attempt to improve on it. Recent analyses by MC-ICP-MS of a large number of chondrites for Hf-isotopic composition and Lu/Hf ratios allowed a new estimate of bulk Earth at $^{176}\text{Hf}/^{177}\text{Hf}=0.282772 \pm 29$ and $^{176}\text{Lu}/^{177}\text{Hf}=0.0332 \pm 2$ (Blichert-Toft and Albarède, 1997); which is a factor of 5 improvement in precision compared to Patchett's early measurements (Patchett and Tatsumoto, 1981). Blichert-Toft and Albarède (1997) used a weighted average of 25 chondrites as choice for bulk Earth and this new value results in bulk Earth being right at the edge the mantle array (see fig. 1) in Hf-Nd-isotope space. If indeed bulk Earth is similar to average chondrite than there must be a "hidden" reservoir in the Earth to compensate for the offset.

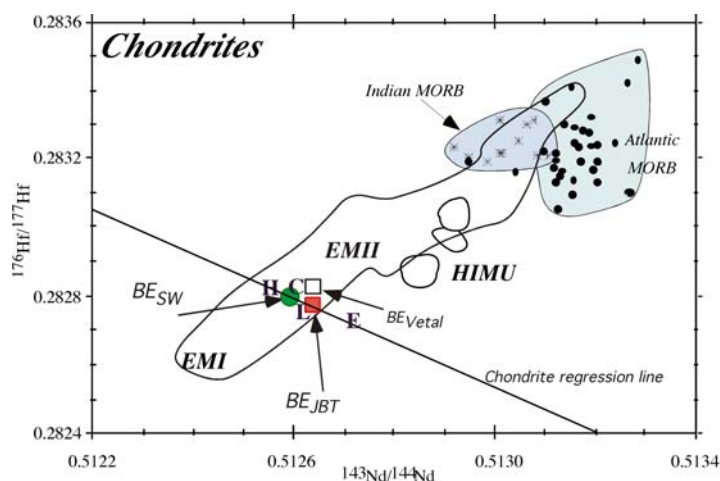


Figure 1: Hf-Nd isotope correlation diagram showing the mantle array and the different values proposed for bulk Earth as well as the average values for the different chondritic classes. Bold letters near the chondrite regression line represent the average for the different classes of meteorites: C= carbonaceous, E= enstatite, H = ordinary high Fe and L = ordinary low Fe. Data for Sm-Nd systematics of the chondrites are from Jacobson and Wasserburg (1980; 1984) and DePaolo (1991), Hf-isotope data for chondrites from Blichert-Toft and Albarède (1997). BE_{SW} is Salters and White value (Salters and White, 1998), BE_{JBT} value is from (Blichert-Toft and Albarède, 1997) and BE_{Vetal} is from (Vervoort et al., 1999).

However, further scrutinizing of the existing chondrite data put in doubt whether a weighted average is indeed the best estimate for bulk Earth (Salters and White, 1998). Salters and White (1998) noted that chondrites when grouped by class form an array in Hf-Nd isotope space that is at a high angle to the mantle array. Salters and White (1998) proposed that bulk Earth is located in the center of the mantle array at the intersection of the mantle and meteorite array and that both the Nd and the Hf-isotopic composition of bulk Earth needed adjustment. Their proposed present-day value would be $^{176}\text{Hf}/^{177}\text{Hf}=0.2828$ and $^{143}\text{Nd}/^{144}\text{Nd}=0.51259$. However, their proposed chondrite array is based on relatively scarce data, only two chondrites have been analyzed from the E class chondrites, but none of them for both Hf and Nd isotopes: Pillistfer for Hf-isotopes and Abee for Nd-isotopes. Only one H-class chondrite has been analyzed for Nd-isotopes (Guareña) and this one has not been analyzed for Hf-isotopes.

Yet a third bulk Earth composition was proposed by Vervoort et al (1999) as an average of the Murchison and Allende carbonaceous chondrites with a value of 0.282833 for $^{176}\text{Hf}/^{177}\text{Hf}$. Because this value is still not in the center of the mantle array they proposed bulk Earth could be even $2\epsilon_{\text{Hf}}$ higher which would obviate the need for a hidden reservoir (Vervoort et al., 1999). If they had suggested the same averaging for the Nd-isotopes, $^{143}\text{Nd}/^{144}\text{Nd}$ of bulk Earth would be 0.51261. However, this combination of Hf and Nd isotope values for bulk Earth 0.282833 and 0.51261 respectively would still not be in the center of the mantle array and further arbitrary adjustment would be needed to avoid the conclusion that there is a “hidden” reservoir.

The estimates suggested by all three groups are based on reasonable assumptions and it is difficult to choose one over the other. The way to resolve this important issue is by combined Hf-Nd isotope analyses of chondrites in order to substantiate the observation by Salters and White (1998) and confirm or deny that such an array does indeed exist.